[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Energy of Immersion of Crystalline Powders in Water and Organic Liquids. I.[1]

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1. Introduction

The energy relations at the surface of a crystalline solid are extremely important but almost wholly unknown. At present there is no known procedure for the determination of the *free* energy of such a surface, but Lipsett, Johnson and Maass,[1a] have devised a method for obtaining what is commonly designated as the *total* surface energy. Their procedure consists of the determination of the heat of solution of extremely fine and very coarse crystals of the substance. The excess in the heat of solution of the fine crystals per unit mass is attributed to their greater surface area. By use of this method the surface energy of sodium chloride was found to be 400 ergs per sq. cm. Similar work by us gave 395 ergs per sq. cm., which is practically the same.

However, this is much higher than the free energy of the sodium chloride surface at the absolute zero as calculated by Lennard-Jones and Dent,[2] on the basis of the theory of Madelung[3] and Born.[4]

The decrease in the *total* surface energy of a solid when it is immersed in any given liquid is less than the total surface energy itself, as is pointed out in connection with the thermodynamics involved, in Paper II. In surface chemistry this decrease is designated as the *energy of immersion* of the solid, and from this the *total energy of adhesion*[5] may be obtained. The measurements needed for the determination of these quantities are of: (1) the heat of immersion of the solid in the liquid, (2) the surface area of the powder, and (3) the surface tension of the liquid and its variation with the temperature.

Although the phenomenon of the evolution of heat when an insoluble, finely divided solid is immersed in a liquid has been known for more than

a century,[6] and has been studied repeatedly since then,[7] the powders used were porous in the sense that the total area available for contact with the liquid was large in comparison with the external area of the particles. This is true with gas mask charcoal or dried silica gel. In much of the earlier work the powders were contaminated by adsorbed films of water before they were immersed, and this reduced the amount of heat liberated.

When attention is paid to the cleanliness of the surface, it is possible in many cases to measure the evolution of heat concomitant with the immersion of a finely divided, crystalline, non-porous solid in a variety of types of liquids. Proof that the heat evolution is caused by a change in the interfacial energies alone may be demonstrated by two experiments. First, it was found that for the same solid in two or more states of sub-division the heat change is directly proportional to the area. Also, in experiments where varying amounts of the same powder were utilized, it was found that the heat evolution was directly proportional to the mass.

In 1930, Harkins and Dahlstrom[8] made determinations of the heats of immersion of certain crystalline solids in water and organic liquids, but did not obtain satisfactory values of the surface areas, so the important heat per unit area was not given. In the present work the areas were determined, more liquids and solids were investigated, and the calorimetric work was made more accurate. The most difficult part of this type of work is not met with in ordinary calorimetry, so it is essential to describe the experimental work in detail. Thus, the powder must be kept extremely dry until it is immersed, and, if an organic liquid is used, both it and the calorimeter must be very dry.

2. Apparatus and Measurement of the Heat of Immersion

The evolution of heat observed upon the immersion of a non-porous, insoluble, crystalline

(1) Original manuscript received February 14, 1940.

(1a) S. G. Lipsett, F. M. G. Johnson and O. Maass, THIS JOURNAL, **49**, 925, 1940 (1927); **50**, 2701 (1928); A. R. Williams, F. M. G. Johnson and O. Maass, *Can. J. Res.*, [5] **13**, 280 (1935).

(2) J. Lennard-Jones and B. M. Dent, *Proc. Roy. Soc.* (London), **A121**, 247 (1928); B. M. Dent, *Phil. Mag.*, [7] **8**, 530 (1929).

(3) Madelung, *Physik. Z.*, **20**, 494 (1919).

(4) M. Born, *Encyklopadie der Math. Wiss.*, **5**, 743 (1923).

(5) Bartell and co-workers [*Ind. Eng. Chem.*, **19**, 1277 (1927)] consider a quantity which they designate as the work or free energy of adhesion, but it is evident from the method employed that the surface of the solid powder is already covered by a film of the liquid before the determination is made. See also: Bangham and Razouk, *Trans. Faraday Soc.*, **33**, 1459 (1937).

(6) Pouillet, *Ann. chim. phys.*, **20**, 141 (1822).

(7) Brown and Mathews [*Colloid Chem.*, **1**, 456 (1926)] list 28 references.

(8) (a) Harkins and Dahlstrom, *Ind. Eng. Chem.*, **22**, 897 (1930); (b) see also A. Clark and B. D. Thomas, *J. Phys. Chem.*, **43**, 579 (1939).

powder is a rapid and well-defined process. Usually the total heat is liberated within two minutes after the immersion of the powder. This feature of the heat evolution made it possible to use general calorimetric methods already developed to a high degree of precision in this Laboratory.[9]

The Calorimeter.—The calorimeters consist of 800 cu. cm. wide-mouth silvered Dewar flasks (Fig. 1) cemented by litharge–glycerol cement to brass rings to which the calorimeter top is bolted. The 36-junction copper–constantan thermel (T), the stirrer (S), the heater (H), and all-glass cooler (C), the glass tube for filling the calorimeter (G), and the support (B) for the wire basket in which the thin-walled glass bulb filled with powder is contained, are all admitted by vapor tight tubes through the cover. The bulb is broken by the action of a screw. A small correction is introduced by the heat of breaking, but the use of the bulb allows the powder to come into thermal equilibrium with the liquid before contact.

The following factors were found to be of primary importance: type and rate of stirring; high accuracy of the measurement of change of temperature; rigorous drying of solids, liquids and the calorimeter, and the transference of liquids under anhydrous conditions; reduction of the error due to evaporation; accurate determination of the electric energy equivalent; and rapid attainment of thermal equilibrium with the calorimeter.

(a) **Stirring.**—The stirrer should be so designed as to cause the rapid disintegration of the aggregates of powder, and to bring the whole interior of the calorimeter to constant temperature, with the minimum production of heat due to stirring itself. The use of the inner tube (X) (Fig. 1), and of two propellers of proper design aided in attaining these ends. To aid in obtaining complete wetting only 5 to 10 g. of powder was used in 650 cu. cm. of liquid. The liquid and powder were usually made to flow upward through X, but with powders which tend to float on the surface, this direction was reversed.

The best rate of stirring was decided upon in each instance by the use of a preliminary experiment with an unsilvered Dewar which permitted observation of the rate of dispersion, together with a calorimetric test of the lack of superheating effects upon immersion of the powder. If the stirring was adequate, it was observed that the heat of immersion, expressed as calories per gram, was independent of the total mass of powder immersed over ranges of mass up to 15 g. in 650 cu. cm. of liquid.[10]

(b) **Temperature Measurement.**—Owing to the necessity of using small amounts of powder and to the small magnitude of the heat of immersion itself, the apparatus for the temperature measurement was made so as to give a high sensitivity. Thirty-six junction copper–constantan thermocouples were utilized with a White double potentiometer and a galvanometer of high voltage sensitivity. One mm. on the galvanometer scale placed at 250 cm. corresponded to 0.00005°. One end of the thermel was

(9) T. F. Young and J. S. Machin, THIS JOURNAL, **58**, 2254 (1936).

(10) In this connection the experiments of P. S. Roller [*J. Phys. Chem.*, **35**, 1133 (1931); **36**, 1202 (1932)] are in point; it is believed that the phenomenon observed in our work is the same, namely, one of the dispersion of aggregates of particles less than one micron diameter.

fitted tightly into a small narrow-mouthed Dewar of about 300-cc. capacity which was shielded externally by means of a thin-walled copper cylinder. Since this vessel remained in the thermostat and was filled with water, it afforded a very constant environment and any rapid slight changes in the thermostat temperature were lagged out. The thermostat was a 250-liter bath of light-bodied oil controlled to within 0.0005° by means of a large mercury regulator used in conjunction with a vacuum tube relay heating circuit.
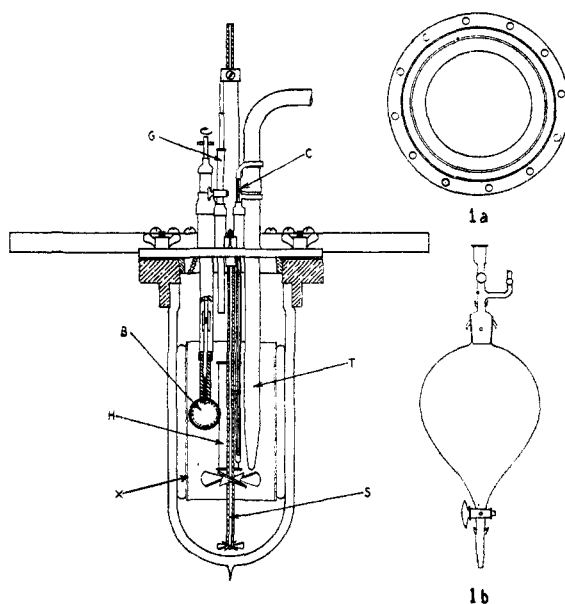

Fig. 1.—Calorimeter: (1a) top of brass ring which is sealed to top of Dewar flask; (1b) funnel used to add dry liquids at G.

(c) **Calorimeter Calibration.**—The temperature change in the calorimeter generated by the immersion of the powder was compared with the temperature increase caused by a known amount of electrical energy which was introduced by a heater (H, Fig. 1). In the experiments reported the agreement between successive values of the electric energy equivalent (calories per microvolt) was within 0.15%. The heating procedure was so arranged that the heater resistance and the heating current could be determined at the time of the heater rating.

(d) **Auxiliary Features.**—Owing to the unusual sensitivity of the heat of immersion to minute amounts of impurities, experiments were usually performed as soon as the calorimeter and its contents could be brought to thermal equilibrium. Often the wetting liquid was initially at a temperature far removed from the thermostat temperature; so if it was inconvenient to wait a sufficient time for the excess heat to leak out through the Dewar jar walls, artificial cooling (cooler C, Fig. 1) was employed. Usually the experiment was begun within one hour after the contents of the calorimeter had been brought to temperature equilibrium.

In order to exclude water, which for this work is without doubt the most important impurity likely to occur in ordinary organic liquids, several precautions were taken in addition to the rigorous purification and drying of the

TABLE I

Compound	Dried by	B. p., °C.	Density d^{20}_4	n^{20}_D	Method of purification or purity
Isooctane	Silica gel	99.33	0.6922	1.3915	Synthetic
Benzene	P_2O_5	80.32	0.8788	....	Ref. a
CCl₄	P_2O_5	76.68	1.5842	....	Ref. b
Et acetate	P_2O_5	77.07	0.9017	....	Na_2CO_3
Nitrobenzene	P_2O_5	210.0	1.2039	....	Recrystn., vac. distn.
Butyl alcohol	Distn.	74.00	0.8089	....	Ref. c
Ethyl alcohol	Silica gel	....	....	....	Ref. c

^{a} Richards and Shipley, THIS JOURNAL, **41**, 2002 (1919). ^{b} Bauer and Daniels, *ibid.*, **56**, 378 (1934). ^{c} Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

liquid itself. To exclude the possibility of contamination by water vapor, the calorimeters were dried thoroughly by passing dry air through them for forty-eight hours. The air, which had been passed previously through towers containing successively soda lime, calcium chloride, anhydrone, sulfuric acid and a five-foot column of phosphorus pentoxide was led into the assembled calorimeter through the glass stirrer shaft, which was a piece of capillary tubing. The air escaped through the glass filling tube (G, Fig. 1). When the stopcock on this tube was closed, sufficient air pressure was built up inside the calorimeter to stop the passage of air entirely. This test served to indicate the tightness of the calorimeter assembly. By use of inter-changeable ground glass joints, the calorimeters were filled with the organic liquids without contact with the air at any time after the final distillation. The vessel used to fill the calorimeters is shown in Fig. 1b. Sometimes, when the purified liquid had been in storage for a length of time previous to the experiment, it was passed over a column of activated silica gel into the calorimeter.

The Materials

(a) **Choice and Treatment of Powders.**—Solids of different types of crystal lattice forces were used in the determinations.

As a result of their large adsorptive forces, solid surfaces nearly always become contaminated with at least a monolayer of water vapor, and possibly other substances, when they are exposed to the atmosphere even for quite short times.[11]

The pre-treatment of the powders was as follows. Five to ten gram samples were placed in heavy-walled Pyrex tubes, the ends of which led to thin-walled glass bulbs. The samples of powder in the heavy-walled tubes were placed in an electric furnace and heated in a high vacuum (10^{-5} mm.) at temperatures from 400 to 600° for twenty-four hours, cooled, and the powder transferred into the thin-walled tubes entirely in high vacuum. The thin-walled, powder-filled tubes were kept in an evacuated jar until the time of the experiment. It is believed that this treatment of the solid surface is adequate to remove practically all water vapor or organic impurities, and that it yields a powder in a standard, reproducible condition.

(b) **Purification of Liquids.**—Great care and much time were devoted to the problem of suitable purification of the various substances utilized. The usual standards of purity such as density, boiling point, freezing point and refractive index, although of indispensable value in fixing

(11) Some of the difficulties in obtaining clean solid surfaces are discussed by Burrage, *Trans. Faraday Soc.*, **28**, 192 (1932).

the degree of purity of the sample, are usually insufficiently sensitive to small amounts of contamination that easily cause large variations in the heat of immersion. The final criterion of purity was the heat of immersion itself and experience indicated that minimum values are to be expected with the most highly purified organic compounds. Some of the relations of the liquids used are outlined in Table I.

The Measurements

The top of the calorimeter was connected to the Dewar jar and the interior vigorously dried for forty-eight hours by a stream of very dry air. At the end of this time, approximately 650 cc. of pure, dry liquid was allowed to run into the calorimeter, which then was placed in an accurately controlled thermostat as quickly as possible and stirring was begun. The contents were brought to temperature equilibrium by means of heating or cooling as proved necessary, and sufficient time was allowed until the slope of the time–temperature curve was not more than 0.1 microvolt per minute. This was usually less than one hour. The temperature of the thermostat was noted and the temperature sensitivity of the thermel determined. Thermel readings were made for twelve consecutive minutes (see Fig. 2) and then the glass capsule was broken by turning the metal compressing screw by means of a glass handle extending through the top of the calorimeter. The exact time at which the powder was immersed in the liquid was noted. After immersion of the powder, thermel readings were continued for sixteen minutes without interruption, then a current was passed through the heater for an exact interval of time (usually three minutes) after which temperature readings were again recorded for twelve more minutes. The purpose of the heating period was to obtain the electric energy equivalent of the calorimeter contents. A second heating period followed by thermel readings for twelve minutes served as a check. If the energy equivalent value did not check to within 0.15%, a third and sometimes a fourth heating period was used. Extrapolations to obtain the exact temperature change were made to the precise time of the immersion of the powder and to the centers of the heating periods. The weight of the powder immersed was determined by difference to milligrams.

3. Heats of Immersion

The values for the heat of immersion are given in Table II. Only one of the six samples of titanium oxide studied is listed. Each of the entries in the table is the average of three or more independent determinations (*i. e.*, fresh quan-
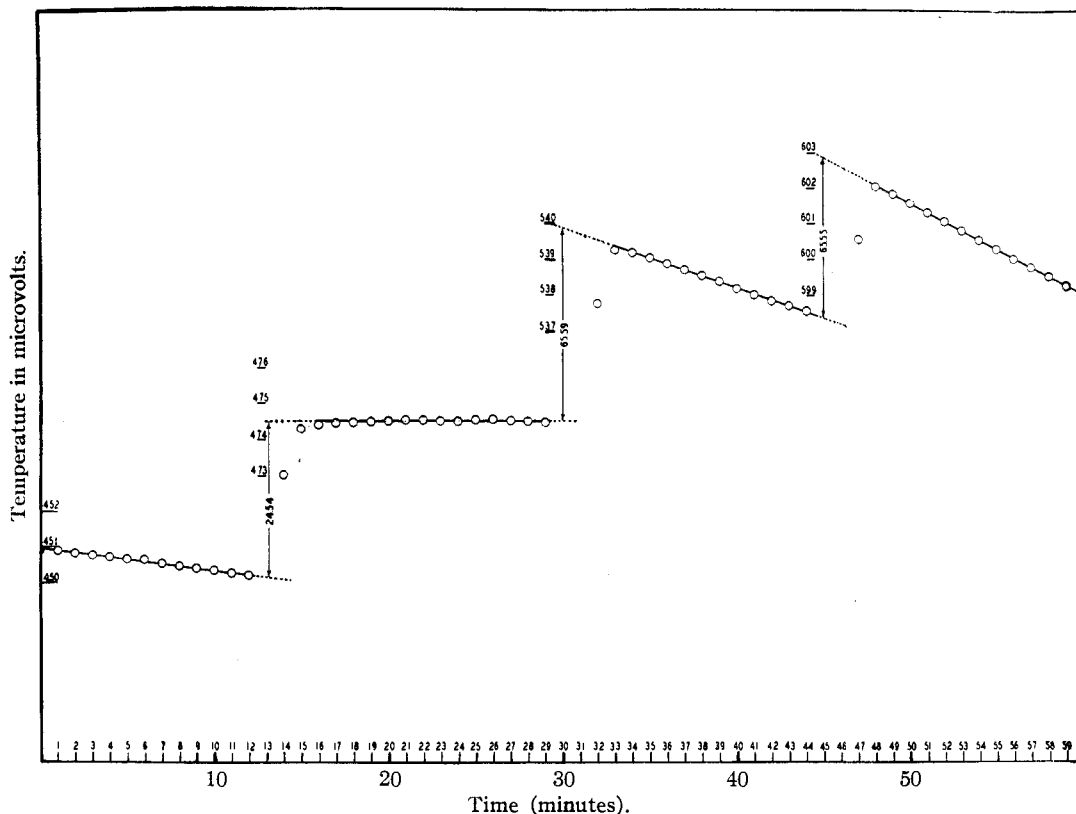
Fig. 2.—Heat of immersion of c. p. titanium dioxide in water at 25°, $\Delta H = 1.797$ cal./g. The rise of temperature on immersion of the anatase powder is represented by an increase of 24.54 microvolts in potential.

tities of liquid); in some cases the values given are the average of as many as twenty determinations. In all of the experiments in which water was the wetting liquid a screw cap top calorimeter was used.[8] This calorimeter was used also with the majority of the liquids to obtain preliminary values. Although an inspection of Table II indicates that the heat of immersion in a non-polar organic substance is roughly one-third that in a more polar wetting liquid, owing to the small specific heats of these non-polar liquids, the actual temperature change noted was often as large and sometimes larger than that for water. The great

likelihood of chance contamination made these heats somewhat less reproducible. The values of Table II are probably good to 2%, although the *precision* of the calorimetery is much higher.

4. Discussion

Table III, in which the heat of immersion of each powder in water is taken as unity, exhibits interesting relations. The ratio of the heat of immersion in benzene, to a non-polar liquid, to that in water is almost the same (0.25 to 0.32) for the oxygen containing solids in the table. With isooctane, another non-polar liquid, the ratio is

TABLE II

HEAT OF IMMERSION OF POWDERS IN VARIOUS LIQUIDS AT 25°

Liquids	TiO₂	ZrO₂	SiO₂	SnO₂	ZnS	BaSO₄	ZrSiO₄	Graphite
	TiO_2	ZrO_2	SiO_2	SnO_2	ZnS	$BaSO_4$	$ZrSiO_4$	Graphite
Water	1.24	0.754	0.334	0.345	(1.31)	0.517	0.562	1.79
Ethyl alcohol	1.20	...	.291	...	...	...	...	1.69
Butyric acid	0.880[8a]							
Ethyl acetate	.850	...	.259	.267	...	.395	...	..
Butyl alcohol	.829	...	.235	.255	...	.375	....	..
Nitrobenzene	.666	.392	...	.239	...	...	.281	..
Carbon tetrachloride	.568	.339	...	.164	...	.236	.270	1.31
Benzene	.351	.241	.084	.111	(0.593)	.147	.174	1.53
Isooctane	.247	.121		.059	...	...	.128	

Header subscript note: columns are SnO_2, ZnS, $BaSO_4$, $ZrSiO_4$. The "Calories per gram of powder" spans the numeric columns.

TABLE III

HEAT OF IMMERSION OF POWDERS IN LIQUIDS: RELATIVE VALUES (WATER = 1.00)

Liquids	TiO_2	ZrO_2	SiO_2	SnO_2	ZnS	$BaSO_4$	$ZrSiO_4$	Graphite
Water	1.00	1.00	1.00	1.00	(1.00)	1.00	1.00	1.00
Ethyl alcohol	0.97	..	0.87	..	..	..	..	0.94
Butyric acid	.77							
Ethyl acetate	.69	..	.78	0.77	..	0.76	..	..
Butyl alcohol	.67	..	.70	.74	..	.73	..	..
Nitrobenzene	.55	0.52	...	.69	..	..	0.50	..
Carbon tetrachloride	.46	.45	..	.48	..	.46	.48	.73
Benzene	.28	.32	.25	.32	(0.46)	.28	.31	.85
Isooctane	.20	.16	..	.17	..	.17	.23	..

constant also (0.17 to 0.23). On this basis these solids may be considered as polar.

With graphite the ratio benzene/water is very much higher (0.85), and this solid may be designated as non-polar. Zinc sulfide occupies an intermediate position (ratio 0.46), but this is probably lower than it should be, due to partial oxidation of the surface.

Summary

1. The heat of immersion (h_i) has been determined for ten solids in from one to nine liquids, and has been found to vary from 0.3 to 1.8 cal. g.$^{-1}$ in water, with smaller values for organic liquids. In paper II of this series the values are given in ergs cm.$^{-2}$ and kcal. mole^{-1}. The most significant relation exhibited is that the ratio $h_i/(h_i)_{H_2O}$ depends almost wholly upon the nature of the liquid for which h_i is determined, and not upon the solid immersed, provided polar liquids only are investigated. For titanium oxide (anatase) the values of the ratio are: water, 1.00; butyric acid, 0.77; ethyl acetate, 0.69; butyl alcohol, 0.67; nitrobenzene, 0.55; carbon tetrachloride, 0.46; benzene, 0.28; isooctane, 0.20. The ratios are almost the same for other oxygen containing solids. These values are almost the same as those obtained earlier by Harkins and Dahlstrom.[8a]

2. The value of the above ratio is very different if the powder consists of a non-polar solid, such as graphite, when the value of h_i for any organic liquid approaches much more closely that for water. For example, in benzene the ratio has a value of 0.28 for titanium oxide, but rises to 0.85 for graphite.

3. The calorimetric determination of the heat of immersion of a crystalline powder involves the following items of technique which are either not involved, or are of minor importance, in the calorimetry of liquids:

a. The powder, the liquid, and the calorimeter must be extremely dry, unless water is the liquid involved, when it is still important to have the powder dry.

b. The surface of the powder must be clean, and the powder and the liquid should be pure.

c. It is essential, after out-gassing the powder in a high vacuum at as high a temperature as will not affect its properties, to transfer the powder to a thin-walled bulb without any exposure to the atmosphere. This transfer was actually made in a high vacuum.

d. The stirring mechanism should be so designed as to produce a maximum dispersion of the powder with a minimum production of heat from the work of stirring.

e. One of the most important requirements, generally neglected, is that the ratio volume of powder to volume of liquid shall be very small